IBM T.J. Watson Research Center

Enhancing Polymers to Achieve Improved Conductivity

In 1993, engineers at the IBM T.J. Watson Research Center believed they were close to a breakthrough in their research into conducting polymers. Conducting polymers, a form of plastic that would carry electric current like metals, were created in the late 1970s, but could not be easily manufactured and, once made, were not stable. Early experiments with acid-doped polyaniline (PANI), one such polymer, produced positive results and indicated that PANI might be able to carry electric current.

The research engineers believed that, with the appropriate acid dopants added to PANI, they could induce a crystalline PANI structure with conductivity similar to copper wire. If the IBM T.J. Watson Research Center succeeded, they would finally bridge the gap between conducting polymer theory and practice. However, IBM's conductivity goal represented a substantial technical risk. Researchers had been trying to reach that goal for nearly 20 years without success.

Given the high risk, company executives would not commit enough funds for the extensive research required to develop PANI. Therefore, the IBM engineers joined with professors at the University of Pennsylvania and the Ohio State University to submit a proposal to the Advanced Technology Program (ATP), and, in 1993, ATP awarded funds for a three-year project.

By the end of the ATP-funded project, the researchers had met some of their goals for developing easily manufactured PANI that could conduct electric current in a fast and stable manner. Specifically, IBM researchers enhanced conductivity, solubility, and thermostability. As a result of this success, executives at the IBM T.J. Watson Research Center invested an additional $4 million for research into PANI. In 1997, the Research Center also licensed a water-soluble version of the polymer to Monsanto, a plastics manufacturing company. Although no products resulted from this licensing effort, Monsanto did find a use for PANI as an anti-corrosion primer.

COMPOSITE PERFORMANCE SCORE

(based on a four star rating)

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Research and data for Status Report 93-01-0149 were collected during January - February 2003.

Decades-Old Material Never Achieved Full Potential

Conducting polymers, a unique class of electronic materials that emerged in the late 1970s, promised many next-generation products. For example, conducting polymers had the potential to allow plastics to replace metals in many applications such as plastic wires and cables, rechargeable batteries, and electronic circuitry for semiconductor applications, as well as shielding against electrostatic discharge and electromagnetic interference. Conducting polymers could not be used in these applications, however, because they were either unstable, difficult to process, or too expensive. They had never reached their full potential of bringing the advantages of plastics to the electronic applications that traditionally required metal.

PANI Promises Advantages Over Other Polymers

In 1993, IBM T.J. Watson Research Center engineers proposed a research plan to bridge the gap between metal-like conductivity and plastic-like flexibility, processability, and recycleability. Initial research on the conducting polymer polyaniline (PANI) showed that it had significant advantages over other polymers. For example, PANI was highly soluble and easy to synthesize, and its properties could be tailored to specific applications. The challenge remained to dope PANI with different acids to dramatically increase its thermal stability and ability to conduct electricity. Much of the prior research had involved changing the overall chemical backbone of conducting polymers without regard to the molecular structure of the polymer. IBM T.J. Watson Research Center engineers believed that the polymer's structure could be the key to enhanced strength and improved characteristics. The engineers believed they could create PANI that had a highly ordered, crystalline structure with the desired properties.

Broad-Based Benefits Would Impact U.S. Economy

The research engineers believed that the benefits from a successful research project would impact the U.S. economy in three stages. During the first stage, the PANI derivative with improved thermal and environmental stability could displace metal and carbon fillers in the aerospace industry by shielding components from potentially dangerous electrostatic discharges. The second stage of economic benefits would be achieved if PANI could be created with increased conductivity. Blends of PANI with other polymers would also have wide applicability for electromagnetic interference shielding in the form of molded structural elements for a variety of products, including computer equipment, consumer electronics, and aerospace structural composites.

Conducting polymers could not be used in many applications because they were either unstable, difficult to process, or too expensive.

A third stage of benefits would occur if the conducting polymers that had enhanced thermal and environmental stability also had conductivity that was close to that of copper. If this were achieved, it would open up a broad range of applications in which PANI could displace metallic conductors or enable new technologies based on its novel properties. For example, hazardous, lead-containing solder used to attach microelectronic components to printed circuits could be replaced with a highly conductive, environmentally safe polymer. Microcircuits could use photo-imageable PANI to replace metal wiring. This same form of PANI could also be used for the circuits that interconnect semiconductor devices.

Internal Funding Unavailable for High-Risk Research

IBM T.J. Watson Research Center engineers decided to pursue a dual-stage research process in order to achieve the proper crystalline form ideal for conductivity. The first step in the process was to design and synthesize dual-functional dopants that would increase the strength of PANI and help the polymer chains self-assemble in a crystalline fashion. The second step would involve the use of dopants that could link across crystalline structures to "lock" the crystalline chains in place for even stronger polymers. Each approach would attempt to strengthen the material and increase its stability. If both succeeded, the engineers believed stability and conductivity would then increase to commercially acceptable levels.

The engineers believed they could create PANI that had a highly ordered, crystalline structure with the desired properties.

The engineers had just begun researching PANI's properties in 1993. In order to carry out parallel research on dual-functional dopants, the Research Center would have been forced to take on risk that was too high for internal funding requirements. Scarce research resources would not be available for a parallel research process. IBM T.J. Watson Research Center engineers felt more could be accomplished with a parallel research program than they could accomplish alone. Therefore, to pursue the parallel research plan, they sought university partners and applied to ATP for support. The university partners included the University of Pennsylvania and the Ohio State University. These professors have specialized expertise in the area of conducting polymers, and, through this project, their students would gain unique industrial research skills in this field.

The goal of the proposed research program was to achieve the properties needed to commercialize conducting polymers. These properties included thermal and environmental stability of the conducting form of the polymer; processability in a variety of solvents, as well as the ability to use several processing techniques to broaden applications; and conductivity over a wide range of conductivity applications, from electrostatic discharge to the high-risk goal of conductivity equivalent to metal. Because these goals were crucially important to industry and required outside funding to focus enough attention on the project to create new, innovative solutions, ATP awarded $1.452 million to conduct parallel research over a three-year period.

Research Engineers Improve PANI and Achieve Project Goals

At the start of the ATP-funded program, the thermal stability of the conducting form of PANI was less than 150°C. The goal by the end of the project was to increase that to 250°C in order to extend PANI's applicability to higher temperature processing and to broaden its use in blends and extrusions such as polycarbonate materials. By using novel, thermally stable dopants, IBM T.J. Watson Research Center engineers reached thermostability in excess of 250°C.

At the project's start, the solubility of the base form of PANI in a common solvent was five percent. Engineers hoped for solubility closer to 20 percent, depending on the structure of PANI that the project ultimately settled upon. The increase in solubility would allow the favorable properties of PANI to permeate the final solvent and give PANI favorable properties. The scientists feared that solutions with greater amounts of PANI (more than 20 percent) would either gel immediately or would have a very limited shelf life, making them unusable for commercial applications. Lower solubility levels (closer to the five-percent industry standard before the ATP-funded project) limited the thickness that could be obtained in a final product, thereby limiting the potential uses for PANI-doped conducting materials. By the end of the research program, engineers had increased solubility to 15 percent, allowing new polymers, copolymers, and blends to be formed that could conduct electricity. This also allowed the development of the first electricity-conducting fibers from PANI.

PANI was unable to conduct much electric current at the start of the project. The high-risk goal of the research program was to enable these plastics to carry enough electric charge to compete with traditional copper wiring. By the end of the project, PANI still could not compete with copper wiring, but conductivity had been increased by 2.5 times. This improvement enormously increased the useful range and applications of these materials.

IBM T.J. Watson Research Center engineers also successfully induced PANI to align into crystalline form during the ATP-funded project. The research showed promise in locking the crystalline chains in place for greater strength. This resulted in $4 million in additional funding from IBM for continued research. The engineers, along with the university partners, continued this research after the close of the ATP-funded program, and their efforts resulted in the licensing of a water-soluble version of PANI to Monsanto Chemical Company to explore creating different insulating materials. While no insulating materials resulted, Monsanto uses PANI as an anti-corrosion primer on other products.

The project generated substantial new knowledge in the field of conducting polymers; resulted in 13 patent applications, 4 copyright applications, 23 presentations, and 31 publications; and led to improvements in conducting polymers' conductivity, solubility, thermostability, and strength.

Conclusion

Engineers at the IBM T.J. Watson Research Center, along with researchers at the University of Pennsylvania and the Ohio State University, collaborated in an ambitious research project to create new polymers that could replace copper conductors in electronic and telecommunications equipment. Though the engineers were unsuccessful in making a polymer with the electrical conductivity of copper, they did improve polyaniline significantly compared to where conducting polymers would have been without ATP support. Moreover, the engineers created a material that was licensed to a plastics manufacturing company. The company has subsequently used the material as an anti-corrosion primer on several products.

PROJECT HIGHLIGHTS
IBM T.J. Watson Research Center

Project Title: Enhancing Polymers to Achieve Improved Conductivity (Three Dimensional Engineering for Advanced Applications)

Project: To develop the basic technology and knowledge base for new conducting polymers with good thermal and environmental stability and an electrical conductivity approaching that of metallic solder.

Duration: 4/1/1994-3/31/1997
ATP Number: 93-01-0149

Funding** (in thousands):

ATP Final Cost	$1,453	73%
Participant Final Cost	539	27%
Total	$1,992	

Accomplishments: IBM T.J. Watson Research Center engineers worked with researchers at the University of Pennsylvania and the Ohio State University to enhance a conducting polymer of doped polyaniline (PANI). PANI represented a substantial improvement over what was available at the start of the ATP-funded research program. Specifically, engineers created PANI with the following improved characteristics that brought the material closer to a commercializeable form:

- Increased thermal stability from 150°C to greater than 250°C, making it possible to manufacture the particular crystalline form and to use it in commercial products
- Increased processability and solubility, but not enough for most commercial applications without additional research
- Increased conductivity by 2.5 times, which showed promise but did not keep up with changing market demand for even more conductivity

The IBM T.J. Watson Research Center also created a water-soluble version of PANI and licensed it to Monsanto Chemical Company. Knowledge gained during the ATP-funded project led to 4 copyright applications, 23 presentations, 31 publications, 13 patent applications, and 11 awarded patents:

- "Deaggregated electrically conductive polymers and precursors thereof"
(No. 5,804,100: filed January 9, 1995; granted September 8, 1998)
- "Methods of fabrication of deaggregated electrically conductive polymers and precursors thereof"
(No. 6,087,472: filed January 9,1995; granted July 11, 2000)
- "Electrically conductive pressure sensitive adhesives"
(No. 5,645,764: filed January 19, 1995; granted July 8, 1997)
- "Methods of fabrication of deaggregated electrically conductive polymers and precursors thereof"
(No. 5,736,623: filed May 30, 1995; granted April 7, 1998)
- "Methods of fabrication of cross-linked electrically conductive polymers and precursors thereof"
(No. 6,030,550: filed February 2, 1996; granted February 29, 2000)
- "Plasticized, antiplasticized and crystalline conducting polymers"
(No. 5,928,566: filed March 22, 1996; granted July 27, 1999)
- "Polycrystalline conducting polymers and precursors thereof having adjustable morphology and physical properties"
(No. 5,932,143: filed March 22, 1996; granted August 3, 1999)
- "Methods of fabricating plasticized, antiplasticized and crystalline conducting polymers and precursors thereof"
(No. 5,969,024: filed March 22, 1996; granted October 19, 1999)
- "Charge transfer complexes between polyaniline and organic electron acceptors and method of fabrication"
(No. 5,776,370: filed April 25, 1996; granted July 7, 1998)
- "Methods of fabricating branched electrically conductive polymers and precursors thereof"
(No. 5,958,301: filed September 27, 1996; granted September 28, 1999)
- "Methods of fabrication of deaggregated electrically conductive polymers and precursors thereof"
(No. 6,005,070: filed January 16, 1997; granted December 21, 1999)

** As of December 9, 1997, large single applicant firms are required to pay 60% of all ATP project costs. Prior to this date, single applicant firms, regardless of size, were required to pay indirect costs.

PROJECT HIGHLIGHTS
IBM T.J. Watson Research Center

Commercialization Status: A water-soluble version of PANI was licensed to Monsanto Chemical Corporation in 1997, and IBM is pursuing further licensing opportunities.

Outlook: According to the IBM T.J. Watson Research Center's final quarterly report issued before the close of the ATP-funded project, the research seemed promising. That positive outlook resulted in $4 million in additional funding from IBM for continued research. Between 1997 and 2003, however, the research has slowed considerably, and the promise of the technology is somewhat muted by changes in market demands. While the polymer research took a large leap forward as a result of the ATP-funded research, IBM will need more licensing partners than the one-time Monsanto license in order to make a commercial impact. The outlook for this technology is uncertain.

Composite Performance Score: * * *

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